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(54) Title: DETERGENT COMPOSITIONS CONTAINING SOIL RELEASE POLYMERS

(57) Abstract

A laundry detergent composition contains a surfactant, sodium tripolyphosphate builder in an amount of at least 5 wt.%, and a soil release polymer which is a defined water-soluble or water-dispersible sulphonated non-end-capped polyester, for example, of terephthalic acid, isophthalic acid, sulphoisophthalic acid and ethylene glycol.

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DETERGENT COMPOSITIONS CONTAINING SOIL RELEASE POLYMERS

TECHNICAL AREA

The present invention relates to laundry detergent compositions containing certain water-soluble or water-dispersible polyesters exhibiting improved soil release properties.

BACKGROUND AND PRIOR ART

Polyesters of terephthalic and other aromatic dicarboxylic acids having soil release properties are widely disclosed in the art, in particular, the so-called PET/POET (polyethylene terephthalate/polyoxyethylene terephthalate) and PET/PEG (polyethylene terephthalate/polyethylene glycol) polyesters which are disclosed, for example, in US 3 557 039 (ICI), GB 1 467 098 and EP 1305A (Procter & Gamble). Polymers of this type are available commercially, for example, as Permalose, Aquaperle and Milease (Trade Marks) (ICI) and Repel-O-Tex (Trade Mark) SRP3 (Rhône-Poulenc). Other patent publications disclosing soil release polymers which are condensation products of aromatic dicarboxylic acids and dihydric alcohols include EP 185 427A, EP 241 984A, EP 241 985A and EP 272 033A (Procter & Gamble).

EP 357 280A (Procter & Gamble) discloses sulphonated end-capped linear terephthalate oligomers which are condensation products of a low molecular weight diol, preferably propylene glycol or ethylene glycol, with terephthalic acid.

The present invention is based on the use of a class of non-end-capped sulphonated polyesters based on dicarboxylic acids and polyols which provide especially effective soil release, especially from polyester fabrics, and which are also effective in reducing soil redeposition in the wash.

DEFINITION OF THE INVENTION

The present invention accordingly provides a detergent composition for washing fabrics, comprising:

(a) from 2 to 50 wt% of an organic surfactant system comprising one or more anionic, nonionic, cationic, amphoteric or zwitterionic surfactants,

(b) from 10 to 80 wt% of a builder component comprising one or more inorganic or organic detergency builders, and comprising at least 5 wt% (based on the detergent composition) of sodium tripolyphosphate,

(c) a soil release effective amount of a water-soluble or water-dispersible sulphonated polyester comprising monomer units of

(i) an unsulphonated aromatic diacidic monomer (A),

(ii) a sulphonated aromatic diacidic monomer (SA)

(iii) optionally a hydroxylated aromatic or aliphatic diacidic monomer (HA), in an amount replacing up to 50 mole% of (A) and/or (SA),

(iv) a polyol (P) selected from ethylene glycol, propylene glycol, isopropylene glycol, glycerol, 1,2,4-butanetriol and 1,2,3-butanetriol, and oligomers of these having from 1 to 8 monomer units,

the polyester having a sulphur content within the range of from 0.5 to 10 wt%;

(d) optionally other detergent ingredients to 100 wt%.

DETAILED DESCRIPTION OF THE INVENTION

The polyesters

The polyesters with which the invention is concerned are defined above. The polyesters and their preparation are disclosed and claimed in WO 95 32997A (Rhône-Poulenc).

Preferred polyesters have the following features:

- the unsulphonated diacidic monomer (A) is an aromatic dicarboxylic acid or an anhydride of a lower (C_1-C_4) alkyl diester thereof, selected from terephthalic acid, isophthalic acid, 2,6-naphthalene dicarboxylic acid, anhydrides and lower (C_1-C_4) alkyl diesters thereof;

- the sulphonated diacidic monomer (SA) is a sulphonated aromatic dicarboxylic acid, anhydride, or lower (C_1-C_4) alkyl diester thereof;

- the mole ratio (A):[(A) + (SA)] is within the range of from 60:100 to 95:100, preferably from 65:100 to 93:100;

- the mole ratio (SA):[(A) + (SA)] is within the range of from 5:100 to 40:100, preferably from 7:100 to 35:100;

- the hydroxylated monomer (HA), if present, is a hydroxylated aromatic dicarboxylic acid, or anhydride or lower (C_1-C_4) dialkyl ester thereof;

- the hydroxylated monomer (HA), if present, does not replace more than 30 mole% of (A) and/or (SA);

- the quantity of (P) is such that the ratio of OH functional groups of (P) to COOH functional groups (or equivalents) of (A) + (SA) + any (HA) is within the range of from 1.05:1 to 4:1, preferably from 1.1:1 to 3.5:1, and more preferably from 1.8:1 to 3:1;

- the polyester has a number average molecular weight of less than 20 000,

- the sulphur content is within the range of from 1.2 to 8 wt%;

- the hydroxyl group content is at least 0.2 OH equivalent per kg of polyester.

The unsulphonated diacidic monomer (A)

As previously indicated, the monomer (A) preferably consists of at least one dicarboxylic acid or anhydride chosen from terephthalic, isophthalic and 2,6 naphthalenedicarboxylic acids or anhydrides or their diesters.

Preferably, monomer (A) is present in a quantity corresponding to a molar ratio (A)/[(A) + (SA)] within the range of from 95:100 to 60:100, preferably from 93:100 to 65:100.

The unsulphonated diacidic monomer (A) preferably consists of 50 to 100 mole%, more preferably 70 to 90 mole%, of terephthalic acid or anhydride or lower alkyl (methyl, ethyl, propyl, isopropyl, butyl) diester, and of 0 to 50 mole%, more preferably from 10 to 30 mole%, of isophthalic acid or anhydride and/or of 2,6-naphthalenedicarboxylic acid or anhydride or lower alkyl (methyl, ethyl, propyl, isopropyl, butyl) diester; the preferred diesters are methyl diesters.

In the unsulphonated diacidic monomer (A) there may additionally be present minor quantities of aromatic diacids other than those mentioned above, such as ortho-phthalic acid, anthracene, 1,8-naphthalene, 1,4-naphthalene and biphenyl dicarboxylic acids or aliphatic diacids such as adipic, glutaric, succinic, trimethyladipic, pimelic, azelaic, sebacic, suberic, itaconic and maleic acids, etc. in the form of acid, anhydride or lower (methyl, ethyl, propyl, isopropyl, butyl) diesters.

The sulphonated diacidic monomer (SA)

Preferably, the sulphonated diacidic monomer (SA) consists of at least one sulphonated aromatic or sulphonated aliphatic dicarboxylic acid or anhydride or lower (C_1-C_4) alkyl diester. Aromatic dicarboxylic acids and their derivatives are preferred.

Preferably, monomer (SA) is present in a quantity corresponding to a molar ratio (SA)/[(A) + (SA)] within the range of from 5:100 to 40:100, more preferably from 7:100 to 35:100.

The sulphonated diacidic monomer (SA) has at least one sulphonic acid group, preferably in the form of an alkali metal (preferably sodium) sulphonate, and two acidic functional groups or acidic functional group equivalents (that is to say an anhydride functional group or two ester functional groups) attached to one or a number of aromatic rings, when aromatic dicarboxylic acids or anhydrides or their diesters are involved, or to the aliphatic chain when aliphatic dicarboxylic acids or anhydrides or their diesters are involved.

Suitable aromatic sulphonated diacidic monomers include sulphoisophthalic, sulphoterephthalic, sulpho-ortho-phthalic acids or anhydrides, 4-sulpho-2,7-naphthalenedicarboxylic acids or anhydrides, sulpho 4,4'-bis (hydroxycarbonyl) diphenyl sulphones, sulphodiphenyldicarboxylic acids or anhydrides, sulpho 4,4'-bis(hydroxycarbonyl) diphenylmethanes, sulpho-5-phenoxyisophthalic acids or anhydrides or their lower (methyl, ethyl, propyl, isopropyl, butyl) diesters.

Suitable aliphatic sulphonated diacidic monomers (SA) include sulphosuccinic acids or anhydrides or their lower alkyl (methyl, ethyl, propyl, isopropyl, butyl) diesters.

The most preferred sulphonated diacidic monomer (SA) is sulphoisophthalic acid in acid, anhydride or diester (preferably dimethyl ester) form, very particularly dimethyl 5-sodiooxysulphonylisophthalate.

The hydroxylated diacidic monomer (HA)

The hydroxylated diacidic monomer (HA), which is optionally present and can replace up to 50 mole%, preferably up to 30 mole%, of (A) and/or (SA), consists of least one hydroxylated aromatic or aliphatic dicarboxylic acid or anhydride or a lower (C1-C4) alkyl diester thereof.

The hydroxylated diacidic monomer (HA) has at least one hydroxyl group attached to one or a number of aromatic rings when it is an aromatic monomer or to the aliphatic chain when it is an aliphatic monomer. Aromatic monomers are preferred.

Suitable hydroxylated diacidic monomers (HA) include 5-hydroxyisophthalic, 4-hydroxyisophthalic, 4-hydroxyphthalic, 2-hydroxymethylsuccinic, hydroxymethylglutaric and hydroxyglutaric acids, in acid, anhydride or lower alkyl diester form.

The polyol (P)

The polyol (P) may be a oligomer comprising up to 8 monomer units, preferably up to 6 and more preferably up to 4 monomer units, but is most preferably a monomer. The polyol is selected from ethylene glycol, propylene glycol, glycerol, 1,2,4-butanetriol, 1,2,3-butanetriol and combinations of these, and their lower (2 to 8, preferably 2 to 6, more preferably 2 to 4) oligomers.

Preferably, the polyol (P) is present in a quantity corresponding to a ratio of the number of OH functional groups of the polyol (P) to the number of COOH functional

groups or functional group equivalents of the total diacidic monomer (A) + (SA) + (HA) within the range of from 1.05:1 to 4:1, preferably from 1.1:1 to 3.5:1 and more preferably from 1.8:1 to 3:1.

The preferred polyols (P) are ethylene glycol and glycerol, ethylene glycol being especially preferred.

Preferably, the sulphonated diacidic monomer (SA) consists of at least one sulphonated aromatic dicarboxylic acid or anhydride or of a mixture of sulphonated aromatic acids or anhydrides and of sulphonated aliphatic acids or anhydrides or their diesters when the polyol (P) does not contain any polyol other than a glycol or when the hydroxylated diacidic monomer (HA) is absent.

Molecular weight

Preferably, the polyester used in accordance with the invention has a number average molecular weight not exceeding 20 000, and preferably not exceeding 15 000.

The molecular weight may be much lower than these limits. Polyesters having molecular weights below 1000, for example, 500-1000, have proved highly effective.

Number average molecular weight may be measured by gel permeation chromatography, for example, in dimethylacetamide containing 10^{-2} N of LiBr, at 25°C, or in tetrahydrofuran. The results are expressed as polystyrene equivalents.

Hydroxyl functional group content

Preferably, the hydroxyl functional group content of the polyester, expressed as OH equivalent/kg of polyester, is at least 0.2. The hydroxyl functional group content may be estimated from proton NMR, the measurement being carried out in dimethyl sulphoxide.

The elementary unit considered in the definition of the mole of monomer (A), (SA) or (HA) is the COOH functional group in the case of the diacids or the COOH functional group equivalent in the case of the anhydrides or of the diesters.

Especially preferred polyesters

An especially preferred polyester is obtainable from the following monomers:

- terephthalic acid (A1) in lower alkyl (preferably methyl) diester form;

- optionally isophthalic acid (A2) in acid or anhydride form;

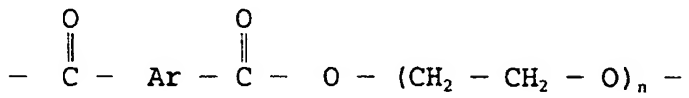
- optionally a hydroxylated terephthalic or isophthalic acid (HA) in acid or anhydride form;

the mole ratio (A1):[(A1) + (A2)] or (A1):[A1 + HA)] or (A1):[(A1) + (A2) + (HA)] being within the range of from 50:100 to 100:100, preferably from 70:100 to 90:100;

- sulphoisophthalic acid (SA), preferably in lower alkyl, preferably methyl, diester form; and

- monoethylene glycol and/or glycerol (P).

Preferred polyesters in accordance with the invention, based on terephthalic acid, isophthalic acid, sulphoisophthalic acid and monoethylene glycol, may be described as having backbone units of the following formula:

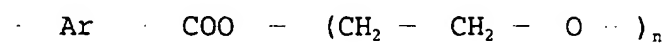


where Ar = terephthalic, isophthalic or sulphoisophthalic, and *n* represents 1, 2, 3 or 4. Typical mole percentages for the different values of n are as follows:

n = 1	58.7
n = 2	30.5
n = 3	8.8
n = 4	1.9,

only trace quantities, if any, of polyethylene oxide units in which n is greater than four being present.

The majority of endgroups are of the formula



wherein n is 1, 2, 3 or 4,

a minority being of the formulae

$$-\text{Ar}-\text{COOH} \qquad \text{or} \qquad -\text{Ar}-\text{COOR}$$

wherein R is a lower alkyl group, preferably methyl.

These polyesters, unlike many disclosed in the prior art, are not end-capped with hydrocarbon or sulphonated capping groups.

Preparation of the polyesters

The polyesters may be prepared by the usual esterification and/or transesterification and polycondensation processes, for example, by esterification and/or transesterification in the presence of a catalyst of the polyol P with the various diacidic monomers (in acid, anhydride or diester form), and polycondensation of the polyol esters at reduced pressure in the presence of a polycondensation catalyst.

A preferred process for the preparation of the polyesters is disclosed and claimed in WO 95 32997A (Rhône-Poulenc).

Detergent compositions

The polyesters are suitably incorporated into detergent compositions in amounts of from 0.01 to 10 wt%, preferably from 0.1 to 5 wt% and more preferably from 0.25 to 3 wt%.

The detergent compositions of the invention also contain, as essential ingredients, one or more detergent-active compounds (surfactants), and a detergency builder system including sodium tripolyphosphate; they may also optionally contain bleaching components and other active ingredients to enhance performance and properties.

The surfactant system

The detergent-active compounds (surfactants) may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

The total amount of surfactant present ranges from 2 to 50 wt%, preferably from 5 to 40 wt%.

Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkylsulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

The polyesters of the present invention are especially suitable for use in compositions containing anionic sulphonate and sulphate type surfactants, for example,

primary alkyl sulphates, alkyl ether sulphates, alkylbenzene sulphonates, and mixtures of these.

According to one preferred embodiment of the invention, the compositions of the invention contain a surfactant system which consists of anionic surfactant only, or of anionic and nonionic surfactants in a weight ratio of at least 0.9:1, preferably at least 1:1. The anionic surfactant is preferably present in an amount of from 5 to 45 wt%, more preferably from 10 to 40 wt%.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

Especially preferred are ethoxylated nonionic surfactants, alkylpolyglycosides, and mixtures of these.

As well as the non-soap surfactants listed above, detergent compositions of the invention may also advantageously contain fatty acid soap.

The detergency builder system

The detergent compositions of the invention also contain a detergency builder system. The total amount of detergency builder in the compositions will suitably range from 5 to 80 wt%, preferably from 10 to 60 wt%.

The builder system contains, as an essential ingredient, sodium tripolyphosphate (STP) in an amount of at least 5 wt%, preferably at least 10 wt%, based on the whole composition.

The STP may be the sole builder present, in which case it is preferably present in an amount of at least 15 wt%, and preferably at least 20 wt%, suitably from 20 to 50 wt%.

Alternatively the STP may be used in combination with one or more other builders, which may be inorganic or organic.

Other inorganic builders that may be present include other phosphate builders, for example, sodium orthophosphate and/or sodium pyrophosphate; sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst).

Especially preferred are combinations of STP with other phosphates, with sodium carbonate, and with sodium aluminosilicate (zeolite). An especially preferred builder system comprises at least 5 wt% of STP in combination with at least 10 wt% of zeolite A.

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. Other zeolites that may be used include zeolites X and Y.

Alternatively, it may be maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070B (Unilever).

Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33. Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00.

Supplementary organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

Detergent compositions according to the invention may also suitably contain a bleach system, which may contain peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution. Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate. The peroxy bleach compound is suitably present in an amount of from 5 to 35 wt%, preferably from 10 to 25 wt%.

The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 1 to 8 wt%, preferably from 2 to 5 wt%.

A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA) and the polyphosphonates such as ethylenediamine tetramethylene phosphonate (EDTMP) and its salts, and diethylenetriamine pentamethylene phosphonate (DETPMP) and its salts.

The present invention is also of especial applicability to non-bleaching compositions suitable for washing delicate fabrics. Such compositions may, for example, have one or more of the following characteristics:

- a 1 wt% aqueous solution pH, in demineralised water, not exceeding 10.5, and preferably not exceeding 10;

- absence, or an extremely low level, of fluorescer;

- presence of a polycarboxylate polymer, for example, an acrylic/maleic copolymer such as Sokalan (Trade Mark) CP5 ex BASF;

- presence of a polymer effective to inhibit dye transfer, for example, polyvinyl pyrrolidone;

- presence of a heavy metal sequestrant, for example, the aminomethylenephosphonic acids and salts such as EDTMP and DETPMP mentioned above in the context of bleach stabilisation.

The compositions of the invention may also contain one or more enzymes. Suitable enzymes include the proteases, amylases, cellulases and lipases usable for incorporation in detergent compositions.

Preferred proteolytic enzymes (proteases) are normally solid, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilisins, which are obtained from particular strains of B. subtilis and B. licheniformis, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

Also suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark) (obtainable from Showa-Denko of Japan), Optimase (Trade Mark) (from Miles Kali-Chemie, Hannover, West Germany), and Superase (Trade Mark) (obtainable from Pfizer of U.S.A.).

Proteases having isoelectric points below 10 include Alcalase, Maxatase, Optimase and Primase (all Trade Marks).

Proteases having isoelectric points of 10 or above include Savinase, Maxacal, Purafect, Opticlean and Esperase (all Trade Marks).

Detergency enzymes are commonly employed in granular form in amounts of from 0.01 to 5.0 wt%.

Other materials that may be present in detergent compositions of the invention include inorganic salts such as sodium carbonate, sodium sulphate or sodium silicate; antiredeposition agents such as cellulosic polymers; fluorescers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; dyes; coloured speckles; perfumes; foam controllers; and fabric softening compounds. This list is not intended to be exhaustive.

Detergent compositions of the invention may be of any suitable physical form, for example, powders or granules, liquids, gels and solid bars.

Detergent compositions of the invention may be prepared by any suitable method. Particulate detergent compositions are suitably prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and then spraying on or postdosing those ingredients unsuitable for processing via the slurry. The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

Particulate detergent compositions of the invention preferably have a bulk density of at least 400 g/l, more preferably at least 500 g/l. Especially preferred compositions have bulk densities of at least 650 g/litre, more preferably at least 700 g/litre.

Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP 340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

EXAMPLES

The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated. Throughout the Examples * denotes a Trade Mark.

Polymers

The polymer in accordance with the invention used (Polymer 1) was a water-soluble sulphonated polyester of terephthalic acid, isophthalic acid, sulphoisophthalic acid and ethylene glycol having the following approximate composition :

- diacidic monomer comprising approximately 77 mole% terephthalate, 3.7 mole% isophthalate, 18.2 mole% sulphoisophthalate;

- ratio of OH groups ex ethylene glycol to COOH groups ex diacid monomers approximately 1.22;

- number average molecular weight, by GPC in tetrahydrofuran at 25°C with calibration against polystyrene standards, 534; weight average molecular weight 1667;

- sulphur content 2.4 wt%;

- hydroxyl group content approximately 1.4-1.5 per kg polyester.

For comparative purposes, the following commercially available polymers were used:

Polymer A: Sokalan (Trade Mark) HP22 ex BASF, a graft copolymer of polyethylene glycol and polyvinyl acetate.

Polymer B: Repel-O-Tex (Trade Mark) ex Rhône-Poulenc, a PET/POET polymer, used in the form of a granule (50% wt% polymer, 50 wt% sodium sulphate).

Polymer C: Aquaperle (Trade Mark) 3991 ex ICI, a PET/POET polymer.

EXAMPLE 1

Phosphate-built particulate detergent compositions were prepared to the following general formulation, using spray-drying and postdosing techniques:

Na linear alkylbenzene sulphonate	5.60
Nonionic surfactant 7EO	4.20
Nonionic surfactant 3EO	3.30
Soap	0.25
Pristerine* 4916 (fatty acid)	0.28
Sodium alkaline silicate	5.60
Sodium tripolyphosphate	22.00
Sodium carbonate	9.00
Sodium carboxymethylcellulose	0.30
Acrylic/maleic copolymer (Sokalan* CP5)	0.97
EDTA (4Na salt)	0.12
Fluorescer	0.16
Sodium sulphate	27.00
Sodium perborate	13.00
TAED	
Soil release polymer (see below)	0 or 0.40
Antifoam granule, enzymes, sodium carbonate, perfume, water to	100.00

Soil release and detergency were measured using radio(^{3}H)-labelled triolein as a soil. The wash regime was as follows: polyester cloths were washed for 20 minutes in Tergotometers in the test formulations (with or without soil release polymer at 0.4 wt%), at the product dosages stated, at 40°C in 24°FH (calcium only) water.

Single wash: soiled cloths were washed as described above.

Prewash: as single wash but no soil present; after prewash the fabrics were rinsed in a beaker with 1 litre of water at 20°C and dried overnight.

Main wash: as for single wash but using pretreated fabrics.

Detergency results

Product dosage: 7.8 g/litre

Polymer (0.4 wt%)	% Detergency	
	Single wash	Prewash + main wash
None	79.1	53.6
Polymer 1	100.0	100.0
Polymer A	86.3	87.1
Polymer B	92.6	100.0
Polymer C	79.1	53.6

EXAMPLE 2

Phosphate-built particulate detergent compositions were prepared to the following general formulation, using spray-drying and postdosing techniques:

Na linear alkylbenzene sulphonate	25.00
Zeolite	1.17
Sodium tripolyphosphate	21.68
Sodium silicate	5.00
Calcium carbonate	10.00
Sodium sulphate	21.24
Sodium carboxymethylcellulose	0.70
Fluorescer	0.01
Acrylic/maleic copolymer (Sokalan* CP5)	1.80
Perfume	0.25
Protease (Savinase* 6T)	0.20
Lipase (Lipolase* 100T)	0.05
Amylase (Termamyl* 60T)	0.08
Antifoam (silicone oil/silica)	0.01
Soil release polymer	see below
Moisture and impurities	to 100.00

The formulations had a bulk density of 420-440 g/litre and a 1 wt% aqueous solution pH in demineralised water at 25°C of 9.7-9.8.

Soil release and detergency on knitted polyester test cloths stained with Oilsol Blue dye/olive oil, were assessed in the tergotometer at two different product dosages, using the following wash regimes:

	3.8 g/l	1.3 g/l
Water hardness	25:3 Ca:Mg	15:3 Ca:Mg
pH	8.45	8.22
Temperature	28°C	
Soak/wash time	30 min soak/10 min wash	
Prewashes	5	
Replicates	2	

Detergency was assessed by measuring reflectance before and after washing using Micromatch (Trade Mark) apparatus. The differences (ΔR 580*) are shown in the following Table:

Polymer	%	3.8 g/l	1.3 g/l
None	0	32.68	22.94
Polymer 1	0.5	57.29	63.02
Polymer A	1.0	50.63	27.96
Polymer B	0.5	52.05	50.41

Stain removal was also assessed visually by an experienced panel of five people. The results, expressed on a scale of 1 (heavy staining, initial stain) to 10 (complete removal), were as follows:

Polymer	%	3.8 g/l	1.3 g/l
Initial	-	1	1
None	0	3	3
Polymer 1	0.5	10	10
Polymer A	1.0	6	4
Polymer B	0.5	8	8

EXAMPLE 3

Further phosphate-built particulate detergent compositions were prepared to the following general formulation, using spray-drying and postdosing techniques:

Na linear alkylbenzene sulphonate	25.00
Sodium tripolyphosphate	22.50
Sodium silicate	5.00
Sodium sulphate	28.90
Sodium carboxymethylcellulose	0.70
Acrylic/maleic copolymer (Sokalan* CP5)	2.00
Sodium carbonate	2.00
Fluorescer speckles	1.00
Citric acid (anhydrous)	3.00
Protease (Opticlean* M375)	0.784
Lipase (Lipolase* 100T)	0.253
Antifoam (silicone oil/silica)	0.04
Perfume	0.33
Soil release polymer	see below
Moisture and impurities	to 100.00

The formulations had a bulk density of 370-430 g/litre and a 1 wt% aqueous solution pH in demineralised water at 25°C of 9.7-9.8.

Detergency was assessed, as in Example 2, by measuring reflectance before and after washing using Micromatch (Trade Mark) apparatus. The differences (ΔR 580*) are shown in the following Table:

Polymer	%	3.8 g/l	1.3 g/l
None	0	30.34	38.56
Polymer 1	0.25	57.84	60.67
Polymer A	1.0	53.23	59.48
Polymer B	0.25	53.71	61.77
Polymer B	0.35	54.50	58.53

Soil release properties were also assessed at a product dosage of 1.3 g/l, by measuring relectance after a first wash and again after a second wash. The wash regime in the tergotometer was as follows:

Test cloth	Knitted polyester
Stain	Oilsol Violet/olive oil
Water hardness	21:6 Ca:Mg
Temperature	28°C
Prewashes	none
Soak/wash time	30 min soak/10 min wash
Rinse time	2 x 2 min

Results

Polymer	%	R 580*			
		Wash 1	Wash 2	Difference	
None	0	42.30	44.49	2.19)	2.70
		43.34	46.55	3.21)	
1	1.0	46.75	58.31	11.56)	12.99
		56.05	70.47	14.42)	
B	1.0	50.45	60.52	10.07)	10.12
		45.58	55.75	10.17)	

EXAMPLE 4, COMPARATIVE EXAMPLES D and E

In these Examples, the effects of Polymers 1 and B in formulations built with STP and with zeolite were compared. The zeolites used were zeolite 4A (Wessalith* P de Degussa) and zeolite P having a Si:Al ratio less than 1.33 (zeolite MAP)(Doucil* A24 ex Crosfield Chemicals).

Ingredients were dosed separately into tergotometers to give the following formulations:

	Parts by weight		
	D	E	4
Sodium linear alkylbenzene sulphonate	20.00	20.00	20.00
Sodium carbonate	25.00	25.00	25.00
Sodium chloride	20.00	20.00	20.00
Zeolite MAP	22.00	-	-
Zeolite A	-	22.00	-
Sodium tripolyphosphate	-	-	22.00
Soil release polymer	---------0 or 1.00-------		

Soil release and detergency on polyester cloths soiled with radio(^{3}H)labelled triolein were measured, as in Example 1, using the single-wash regime described in Example 1 (20 minutes, 25°C, 24°FH (calcium only) water). The "product" dosage was 1.5 g/l. The results were as shown overleaf.

In all three compositions Polymer 1 caused a significant detergency increase. Polymer B caused smaller detergency increases in the two zeolite formulations, but in the STP formulation the presence of Polymer B actually

brought about a substantial fall in detergency, while the presence of Polymer 1 caused a comparable rise in detergency.

The difference between the effects of the two polymers was most marked in the STP formulation.

Comparative Example D: zeolite MAP

	Detergency	Polymer benefit
No polymer	29.6	
Polymer 1	56.7	27.1
Polymer B	37.2	7.6

Benefit of Polymer 1 over Polymer B = 19.5

Comparative Example E: zeolite 4A

	Detergency	Polymer Benefit
No polymer	50.0	
Polymer 1	73.8	23.8
Polymer B	62.0	12.0

Benefit of Polymer 1 over Polymer B = 11.8

Example 4: Sodium tripolyphosphate

	Detergency	Polymer Benefit
No polymer	63.1	
Polymer 1	75.3	12.2
Polymer B	50.8	-12.3

Benefit of Polymer 1 over Polymer B = 24.5

EXAMPLES 5 to 7

Examples of phosphate-built non-bleaching high bulk density particulate detergent compositions containing soil release polymers of the invention are as follows:

	5	6	7
Na LAS[1]	28.66	24.70	15.00
Na PAS[2]	2.88	4.19	-
Nonionic 9EO	-	-	2.51
Zeolite	18.84	21.31	6.24
Na tripolyphosphate	29.69	6.78	39.25
Na carbonate	-	16.43	23.52
Na bicarbonate	6.26	-	2.97
Na silicate	-	-	2.37
SCMC	0.78	0.78	0.57
Fluorescer	0.01	0.56	0.30
Copolymer (Sokalan* CP5)	1.93	1.99	1.18
Protease (Savinase* 6T)	0.32	0.40	0.70
Lipase (Lipolase* 100T)	0.08	0.10	0.26
Amylase (Termamyl* 60T)	0.14	-	-
Soil release polymer	0.50	0.50	0.50
Perfume	0.40	0.40	0.60
Moisture and impurities	-----	to 100.00	----
Bulk density (g/litre)	780-820	ca. 800	ca. 800

[1]Sodium linear alkylbenzene sulphonate
[2]Sodium primary alcohol sulphate

The composition of Example 5 is of low solution pH (9.7-9.8) and is especially suitable for washing delicate fabrics.

EXAMPLE 8

A further example of a high bulk density non-bleaching phosphate-built powder of low solution pH in accordance with the invention, suitable for washing delicate fabrics, is as follows:

Na LAS	6.50
Nonionic 6/7EO	4.00
Soap	4.30
Na tripolyphosphate	29.17
Na silicate	10.00
SCMC	0.43
Polyvinyl pyrrolidone	0.95
Na sulphate	17.00
Na carbonate (heavy)	6.00
Ammonium sulphate	2.00
Citric acid	2.25
Na metasilicate	2.00
Amorphous aluminosilicate	1.12
Protease (Savinase* 6T)	0.20
Lipase (Lipolase* 100T)	0.05
Amylase (Termamyl* 60T)	0.25
Cellulase (Celluzyme* 0.7T)	0.40
Soil release polymer	0.55
Perfume	0.40
Moisture and impurities	to 100.00

The bulk density of this formulation is 700 g/litre and the 1 wt% aqueous solution pH in demineralised water is 9.7-9.8.

EXAMPLES 9 and 10

Examples of high bulk density phosphate-built bleaching particulate detergent compositions in accordance with the invention are as follows:

	9	10
Na LAS	6.50	9.00
Nonionic 6/7EO	4.00	4.00
Soap	4.30	-
Na tripolyphosphate	28.40	30.00
Na silicate	10.00	10.00
SCMC	0.36	0.36
Fluorescer	0.20	0.20
EDTA	0.06	0.06
Na carbonate (heavy)	18.50	18.72
Citric acid	2.25	2.25
Na perborate $4H_2O$	8.55	8.55
TAED	2.08	2.08
Amorph. aluminosilicate	0.86	0.97
Protease (Savinase* 4.8T))	0.65	1.00
Lipase (Lipolase* 100T))		
Soil release polymer	0.55	0.55
Perfume	0.40	0.40
Moisture and impurities	---- to 100.00	-----
Bulk density (g/litre)	700	700

EXAMPLES 11 and 12

Examples of phosphate-built spray-dried non-bleaching particulate detergent compositions in accordance with the invention containing high levels of anionic surfactant are as follows:

	11	12
Na LAS	26.00	26.00
Na tripolyphosphate	26.00	26.00
Na alkaline silicate	9.00	9.16
Sodium sulphate (in base)	14.57	9.71
SCMC	1.00	1.00
Fluorescer	0.25	0.25
Sodium carbonate	10.00	10.00
Sodium sulphate (postdosed)	-	6.41
Enzyme (Maxacal* 600000)	0.14	0.20
Soil release polymer	0.50	0.50
EDTA, colour, nonionic surfactant, water, perfume	----- to 100.00 -----	
Bulk density (g/litre)	365-435	365-435

EXAMPLES 13 and 14

Examples of phosphate-built high bulk density non-bleaching particulate detergent compositions in accordance with the invention containing high levels of anionic surfactant are as follows:

	13	14
Na LAS	26.00	26.00
Na tripolyphosphate	26.00	26.00
Na alkaline silicate	9.53	9.53
Sodium sulphate (in base)	12.52	12.52
SCMC	1.04	1.04
Fluorescer	0.26	0.26
Sodium carbonate	8.47	8.53
Zeolite A (as hydrated)	3.00	3.00
Enzymes: Savinase*/Lipolase*	0.50	0.50
Soil release polymer	0.50	0.50
Perfume	0.25	0.30
EDTA, colour, water etc	----- to 100.00 ----	
Bulk density (g/litre)	720-800	720-800

EXAMPLE 15

An example of a high bulk density phosphate-built bleaching particulate detergent composition in accordance with the invention containing a high level of anionic surfactant is as follows:

Na LAS	26.355
Na tripolyphosphate	24.478
Na alkaline silicate	8.931
Sodium sulphate (in base)	8.215
SCMC	0.938
Fluorescer	0.149
Sodium carbonate	5.365
Zeolite A (as hydrated)	3.576
Sodium perborate (monohydrate)	7.294
TAED green granules	2.824
EDTMP (Dequest* 2047)	0.471
Enzymes: Savinase*/Lipolase*	0.224
Kazusase*	0.224
Soil release polymer	0.500
Perfume	0.300
EDTA, colour, water etc	to 100.00
Bulk density	720-800 g/litre

EXAMPLES 16 and 17

Further examples of phosphate-built non-bleaching particulate detergent compositions in accordance with the invention, one spray-dried and the other of high bulk density, are as follows:

	16	17
Na LAS	6.50	11.25
Na tripolyphosphate	28.00	39.25
Na alkaline silicate	9.00	4.13
Sodium sulphate (in base)	24.30	5.42
EDTA	0.01	0.004
SCMC	1.00	1.00
Fluorescer	0.38	0.38
Nonionic surfactant 7EO	3.00	5.00
Soap	5.00	-
Antifoam granule	-	2.00
Sodium carbonate	12.00	22.68
Enzymes: Savinase*/Lipolase*	0.22	0.70
Soil release polymer	0.50	0.50
Perfume	0.15	0.30
EDTA, colour, water etc	----- to 100.00 ----	
Bulk density (g/litre)	375-425	760-840

EXAMPLE 18

An example of a phosphate- and carbonate-built spray-dried particulate detergent composition in accordance with the invention containing a high level of anionic surfactant, a bleach system and a photobleach, is as follows:

Na LAS	22.00
Na carbonate (heavy)	15.00
Na tripolyphosphate	13.30
Na alkaline silicate	7.30
Na sulphate	22.30
Na perborate	8.00
TAED	2.40
SCMC	0.35
EDTMP	0.40
Protease (Savinase* 6T)	0.65
Lipase (Lipolase* 100T)	0.13
Fluorescer	0.20
Cu phthalocyanine	0.011
Soil release polymer	0.50
Perfume	0.25
Moisture and impurities	to 100.00

Bulk density 460 g/litre

EXAMPLES 19 and 20

Examples of high bulk density non-bleaching particulate detergent compositions in accordance with the invention containing mixed zeolite, phosphate and carbonate builders are as follows:

	20	21
Na LAS	18.00	22.00
Nonionic 7EO	1.60	2.00
Na soap (stearate)	-	2.00
Na tripolyphosphate	22.50	28.00
Zeolite A (anhydrous basis)	8.00	12.00
Na carbonate	25.00	27.00
Fluorescer	0.12	0.12
SCMC	0.55	0.55
Na sulphate	19.50	0.49
Savinase* 6.0T/Lipolase* 100T	0.75	0.75
Soil release polymer	0.50	0.50
Perfume	0.35	0.35
Moisture and minor ingredients	----- to 100.00 -----	
Bulk density (g/litre)	850	840

* * *

CLAIMS

1 A detergent composition for washing fabrics, comprising:

(a) from 2 to 50 wt% of an organic surfactant system comprising one or more anionic, nonionic, cationic, amphoteric or zwitterionic surfactants,

(b) from 10 to 80 wt% of a builder component comprising one or more inorganic or organic detergency builders,

(c) a soil release effective amount of a water-soluble or water-dispersible soil release polymer,

(d) optionally other detergent ingredients to 100 wt%,

characterised in that the detergent builder component (b) comprises at least 5 wt% (based on the detergent composition) of sodium tripolyphosphate, and the soil release polymer (c) is a water-soluble or water-dispersible sulphonated polyester comprising monomer units of

(i) an unsulphonated aromatic diacidic monomer (A),

(ii) a sulphonated aromatic diacidic monomer (SA)

(iii) optionally a hydroxylated aromatic or aliphatic diacidic monomer (HA), in an amount replacing up to 50 mole% of (A) and/or (SA),

(iv) a polyol (P) selected from ethylene glycol, propylene glycol, isopropylene glycol, glycerol, 1,2,4-butanetriol and 1,2,3-butanetriol, and oligomers of these having from 1 to 8 monomer units,

the polyester having a sulphur content within the range of from 0.5 to 10 wt%.

2 A detergent composition as claimed in claim 1, characterised in that it comprises from 0.01 to 10 wt% of the polyester (c).

3 A detergent composition as claimed in claim 2, characterised in that it comprises from 0.1 to 5 wt% of the polyester (c).

4 A detergent composition as claimed in any preceding claim, characterised in that it comprises from 5 to 50 wt% of sodium tripolyphosphate.

5 A detergent composition as claimed in any preceding claim, characterised in that it comprises at least 10 wt% of sodium tripolyphosphate.

6 A detergent composition as claimed in claim 5, characterised in that it comprises from 20 to 50 wt% of sodium tripolyphosphate.

7 A detergent composition as claimed in any one of claims 1 to 5, characterised in that the detergency builder system further comprises one or more additional inorganic builders selected from sodium orthophosphate, sodium pyrophosphate, sodium carbonate, zeolite A and zeolite MAP.

8 A detergent composition as claimed in any preceding claim, characterised in that the organic surfactant system comprises a sulphate or sulphonate type anionic surfactant optionally in combination with a nonionic surfactant.

9 A detergent composition as claimed in claim 8, characterised in that the anionic surfactant comprises primary alkyl sulphate and/or alkyl ether sulphate and/or alkylbenzene sulphonate.

10 A detergent composition as claimed in any preceding claim, characterised in that it is particulate and has a bulk density of at least 650 g/litre.

* * *

INTERNATIONAL SEARCH REPORT

International Application No
PC./EP 96/04994

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
27 March 1997	11.04.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Grittern, A

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INTERNATIONAL SEARCH REPORT

Inter ›onal Application No
PC›/EP 96/04994

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